

Photoluminescence from Porous Silicon by Infrared Multiphoton Excitation

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Visible photoluminescence from porous silicon induced by infrared multiphoton excitation was observed at room temperature. Luminescence resulted from carrier excitations in the surface region of the sample. With the pump in the mid-infrared, excitation was effective only when the pump frequency was near resonance with the stretch vibrations of the surface species, SiH_x . For each visible photon emitted, at least seven or eight infrared photons were absorbed. The excitation is believed to occur via pumping up a vibrational ladder, followed by conversion to electronic excitation. The process is similar to infrared multiphoton excitation of polyatomic molecules.

The observation that efficient visible photoluminescence (PL) from porous silicon can be induced at room temperature has stimulated intense research (1) in recent years, because the effect could lead to the development of silicon-based luminescing devices. However, in all previous experiments, PL was induced by direct excitations of the carriers. Now we show that PL can be induced in porous silicon by infrared multiphoton excitation (MPE) via surface electronic states as well as via SiH_x stretch vibrations at the surfaces of the porous Si. This finding provides direct proof that surface electronic states or surface vibrational modes can be involved in the excitation of the PL. With the pump wavelength in the mid-infrared, an absorption of seven to eight pump photons is needed for emission of one visible luminescent photon. The excitation is effective only when the pump frequency is near resonance with the stretch vibrations of SiH_x . The process is similar to infrared MPE of polyatomic molecules, such as SF_6 (2), Si clusters (3), and *n*-butylsilane (4), which results in molecular dissociation and luminescence. The latter has long been a subject of interest in molecular physics and chemistry (5), but to our knowledge, the same effect in a solid has never been reported. Wang *et al.* (6, 7) recently observed three-photon excitation of PL in porous Si. However, they argued that this results from a two-step process, in which third-harmonic radiation is first generated in the porous samples, followed by one-photon absorption of the third-harmonic radiation to produce the luminescence.

The porous Si layers used for this study were prepared by anodic etching of (100) p-type crystalline (c-Si) wafers followed by aging in air as described in (8). They were characterized by Fourier transform infrared

(FTIR) spectroscopy, steady-state and time-resolved PL, and photothermal deflection spectroscopy (PDS). The results showed that the Si layers resemble those commonly studied by others, with a PL quantum efficiency of ~5%. The samples are stable and yield reproducible luminescence. The FTIR spectra indicated that the samples have SiH_x , SiO_x , and OSiH_x species coexisting on the surface (9). The absorption edge measured by PDS showed a long tail with significant absorption below the bulk indirect absorption gap $E_g(\text{c-Si}) = 1.1 \text{ eV}$ (Fig. 1) (8).

For the infrared MPE-PL experiment, we used a tunable infrared source composed of an optical parametric amplifier pumped by an active-passive mode-locked Nd-YAG (yttrium-aluminum-garnet) laser (10). The focused laser intensity on the sample could be varied. Typically, the measurements were carried out at 1 GW/cm^2 , but up to 3 GW/cm^2 no degradation of the PL or damage to the samples was observed. The PL spectra were collected by a monochromator and a photomultiplier (sensitive in the range from 250 to 850 nm) and recorded by a gated electronic system. The PL could be measured with a time delay (after pumping) from 100 ns to 100 μs . The PL spectra were normalized by the spectral response of the monochromator and photomultiplier system. All

MPE-PL measurements were performed in air and at room temperature.

Red PL spectra excited by laser pulses from 0.532 to $4.9 \mu\text{m}$ (Fig. 2) are very similar to each other and to the PL spectrum obtained by ultraviolet excitation above the direct gap of c-Si (Fig. 1). A single luminescence peak appears in the 600- to 900-nm range (11). The emission of a single photon at 700 nm (1.77 eV) requires the absorption of at least one, two, two, and seven photons at 0.532, 1.06, 1.3, and $4.9 \mu\text{m}$ (2060 cm^{-1}), respectively, in the excitation process. The excitation wavelength of $4.9 \mu\text{m}$ is in the region of resonance absorption of the SiH_x stretch vibrations, suggesting that the excitation here could occur by infrared MPE via the vibrational ladder, a process resembling infrared MPE in polyatomic molecules (5). For excitation with shorter wavelengths, the resonances involved must be electronic. There are slight characteristic differences between the electronically and vibrationally excited PL. The latter is blue-shifted by $\sim 100 \text{ cm}^{-1}$ (Fig. 2) and has a faster decay (Fig. 3).

For the 1.06- and $1.3\text{-}\mu\text{m}$ excitations, the one-photon absorption is weak (Fig. 1). However, a direct two-photon step can resonantly excite the sample to the broad "Urbach tail" region (8). Further excitation of the excited carriers to higher electronic states by one-photon resonant steps could be achieved with sufficiently strong input radiation. If the overall excitation is limited by the first two-photon step, the excited carrier density would be proportional to I_{in}^2 , where I_{in} is the input beam intensity (5). If the total luminescence output S is proportional to the excited carrier density, we would expect $S \propto I_{\text{in}}^2$. For pumping at $1.06 \mu\text{m}$ [corresponding to a photon energy of 1.16 eV, higher than the indirect bulk energy gap $E_g(\text{c-Si}) = 1.1 \text{ eV}$ of crystalline Si at room temperature] and at $1.3 \mu\text{m}$ (photon energy of 0.95 eV), this behavior is observed (Fig. 4). This result is clearly different from that obtained by Wang *et al.* (6,

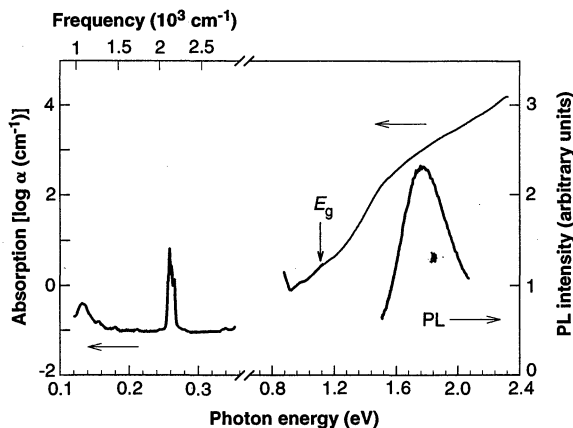


Fig. 1. Absorption spectrum of porous Si showing the vibrational resonances in the 0.1- to 0.4-eV range and the electronic absorption edge in the 0.8- to 2.3-eV range, and photoluminescence (PL) spectrum resulting from 3.5-eV excitation.

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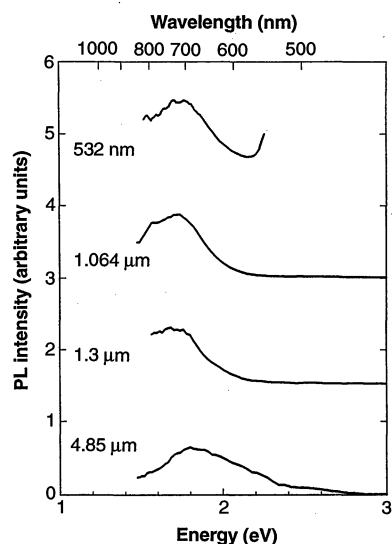


Fig. 2. PL spectra of porous Si observed by excitation at various infrared and visible wavelengths.

7). In their somewhat different porous Si samples, they observed a luminescence band at about 550 to 650 nm, and a luminescence output $S \sim I_{in}^3$ with pumping at 1.064 μm , which they interpreted as luminescence from single-photon excitations by third-harmonic radiation generated in the core of the crystallites. Given our results, we conclude that the luminescence observed by Wang *et al.* (6, 7) may have resulted from direct three-photon excitations. Because second-harmonic generation is not allowed in bulk Si, we cannot expect to find luminescence resulting from single-photon excitation by second-harmonic radiation generated in our samples.

For the 4.9- μm excitation, the $\sim I_{in}^5$ dependence of luminescence output on the input intensity (Fig. 4) is a qualitative indication that the MPE process is of much higher order than for excitation at shorter wavelengths. To confirm that the SiH_x stretch vibrations are involved in the MPE, we scanned the pulsed infrared radiation

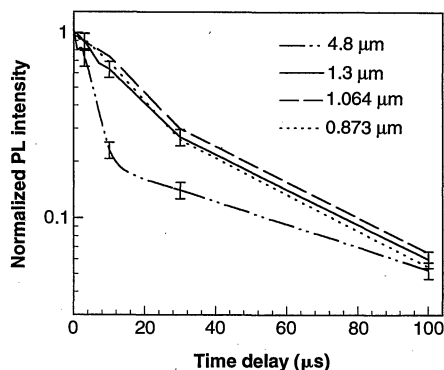


Fig. 3. Decay of the PL output from porous Si excited at different wavelengths.

over the SiH_x and OSiH_x vibrational resonances in the region from 1900 to 2260 cm^{-1} . The vibrational absorption spectrum of the sample (Fig. 5A) exhibits a broad band at $\sim 2120 \text{ cm}^{-1}$ due to surface SiH_x species and a peak at $\sim 2260 \text{ cm}^{-1}$ due to OSiH_x species. The latter resulted from oxidation of our sample, because it was left in air for an extensive period before and during the measurement. For low-excitation intensity (Fig. 5B), the excitation spectrum of the MPE-PL follows the spectral feature of SiH_x fairly closely, but does not reproduce the OSiH_x peak. Further studies on oxidized and unoxidized samples are planned to confirm the latter observation. Here, we focus only on the features connected with the SiH_x vibrations.

The close resemblance of the excitation spectrum of the MPE-PL to the SiH_x vibrational spectrum provides direct evidence that MPE involves SiH_x vibrational excitations. With increasing excitation intensity, however, the broad peak of the excitation spectrum begins to split into two (Fig. 5D); the weaker intensity peak remains unshifted at $\sim 2200 \text{ cm}^{-1}$, whereas the other shifts significantly to lower frequencies. To qualitatively understand these results, we can resort to the generic model of infrared MPE of polyatomic molecules.

For a polyatomic molecule, the excited vibronic (or ro-vibronic) states in the low-excitation range are discrete, but as the density of states increases rapidly with increasing energy, they form a quasi-continuum. At low intensities, a monochromatic beam can resonantly excite the molecule to the first excited ro-vibronic states, but subsequent resonant excitations to higher excited states are less likely because they are rendered off-resonant by the existence of vibrational anharmonicity. At sufficiently high beam intensities, however, direct MPE of the molecule to the quasi-continuum via resonant or near-resonant steps up the vibrational ladder can become significant. Once the molecule reaches the quasi-continuum, it can be readily pumped further up by single-photon resonant steps (because of the rapid increase of the density of states with energy) until it reaches a level where it can cross over to the electronic excited states or molecular dissociation states. In the former case, luminescence may result because the electronic excitation decays radiatively. In this model, the overall MPE that results in luminescence or molecular dissociation is limited by the first MPE step to the quasi-continuum. If this step is an m -photon process, then the luminescent output or dissociation probability is expected to be proportional to I_{in}^m .

We can use the same model to qualitatively explain the observed infrared MPE-

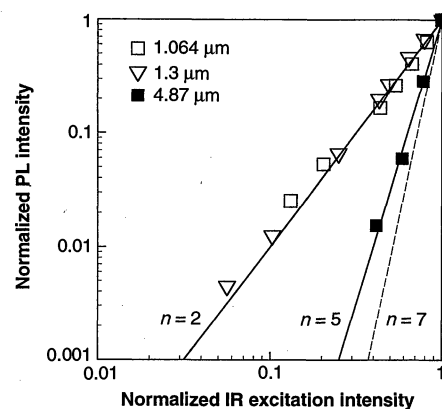


Fig. 4. PL intensity versus excitation intensity at different infrared excitation wavelengths.

PL in porous Si. Here, porous Si is conceptualized as many weakly connected quantum-sized clusters of Si (8). The surface of each cluster is terminated by SiH_x or OSiH_x . The absorption spectrum around the band edge (Fig. 1) is affected by the quantum-size effect. The long "Urbach tail" in the spectrum arises from transitions between band states and surface states. The luminescence arising from reverse transitions peaks at the low-energy end of the absorption tail. As shown above, luminescence can result from direct MPE of carriers into the "Urbach tail" region through use of 1.06- and 1.3- μm radiation. However, the luminescence induced by infrared MPE via vibrational resonances strongly suggests that surface species are involved in the process. Like infrared MPE of polyatomic molecules, the overall excitation here consists of a direct MPE to the vibrational quasi-continuum, followed by a series of

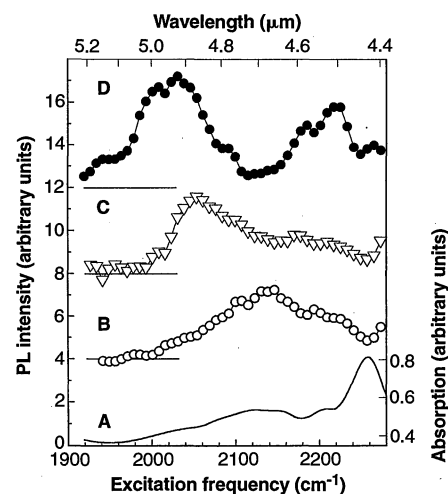


Fig. 5. (A) Vibrational absorption spectrum of porous Si sample under study. (B to D) Excitation spectra of the MPE-PL in the SiH_x stretch vibrational range for pump intensities of (B) 0.4, (C) 0.8, and (D) 2.8 GW/cm^2 .

one-photon resonant steps to sufficiently high levels at which electron-vibration coupling allows effective conversion of vibrational excitation to electronic excitation. The radiative decay of the electronic excitation then results in the observed luminescence. Our preliminary results indicate that MPE is effective only when it occurs via the vibrational ladder of SiH_x but not via the OSiH_x stretch ladder.

There are substantial differences between the problem encountered with porous Si and the commonly studied MPE of polyatomic molecules. Each Si cluster consists of a large number ($\geq 10^6$) of Si atoms that form a core and a large number ($\sim 10^4$) of H atoms passivating its surface (8). The valence electrons in the nanocrystal are delocalized. The SiH_x stretch peaks in the vibrational spectrum are certainly inhomogeneously broadened, and their vibrational lifetimes could be much longer than the 8- to 25-ps pump pulsewidth used in our experiment. The higher excited states of the SiH_x vibrations should have shorter lifetimes. However, only when their lifetimes become shorter than the pump pulsewidth can they be considered to be effectively coupled with other vibrational modes of the system to form a quasi-continuum with a density of states that increases rapidly with energy. The observed I_{in}^5 dependence of the luminescence output from our porous Si sample at long excitation wavelengths suggests that the effective quasi-continuum starts at ~ 1.25 eV, because it takes a direct five-photon absorption of ~ 4.9 - μm (0.25 eV) radiation to reach the quasi-continuum. An overall seven- to eight-photon absorption is needed to induce a single luminescent photon at 600 to 700 nm.

For the observed excitation spectra in Fig. 5, we offer the following explanation. The excitation spectrum, $F(\omega)$, of a five-photon excitation process up a vibrational ladder can be described by

$$F(\omega) = \int P(\{\gamma\}) \prod_{i=0}^4 G_{i \rightarrow i+1}(\omega, \{\gamma\}) d\{\gamma\}$$

where ω is the angular frequency, $G_{i \rightarrow i+1}(\omega)$ is the homogeneous lineshape of the vibrational transition from $v = i$ to $v = i + 1$, $\{\gamma\}$ is a set of parameters describing the local environment, and $P(\{\gamma\})$ is the distribution function of $\{\gamma\}$. We expect the linewidth of $G_{i \rightarrow i+1}(\omega)$ to increase appreciably with the increase of i and pump intensity because of power broadening. If the vibrational anharmonicity is large, with only weak overlap between $G_{i \rightarrow i+1}(\omega)$ and $G_{i+1 \rightarrow i+2}(\omega)$, then the peak of $F(\omega)$ is dominated by $G_{0 \rightarrow 1}(\omega)$. This is the case for MPE at low pump intensities (Fig. 5). If with higher pump intensities, the overlap between

$G_i \rightarrow i+1(\omega)$ and $G_{i+1 \rightarrow i+2}(\omega)$ due to power broadening becomes significant, then the peak of $F(\omega)$ should experience a red shift. This is the case of MPE via the vibrational modes at about 2110 cm^{-1} (Fig. 5). In the latter case, an alternative explanation is that the homogeneous linewidth is always larger than the anharmonic shift, but this is not likely considering that the known anharmonicity of SiH-stretch vibration for H/Si(111) is $\sim 70 \text{ cm}^{-1}$ (12).

We expect MPE-PL to be a generic process that could occur in many semiconductor clusters. Efficiency of MPE-PL via pumping up a vibrational ladder depends on the character of the vibrational mode and its coupling with the carrier excitation.

REFERENCES AND NOTES

1. Materials Research Society meetings in Boston and San Francisco and European Materials Research Society meeting in Strasbourg since 1991.
2. Aa. S. Sudbø, P. A. Schultz, E. R. Grant, Y. R. Shen, Y. T. Lee, *J. Chem. Phys.* **68**, 1306 (1978).

3. L. A. Bloomfield, M. E. Geusic, R. R. Freeman, W. L. Brown, *Chem. Phys. Lett.* **121**, 33 (1985).
4. R. I. McKay et al., *J. Chem. Phys.* **95**, 1688 (1991).
5. See, for example, Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1985), chap. 23.
6. J. Wang et al., *Phys. Rev. Lett.* **69**, 3252 (1992).
7. X. Wang, in *Porous Silicon*, Z. Chuan and R. Tsu, Eds. (World Scientific, River Edge, NJ, 1994), pp. 77-98.
8. F. Koch, V. Petrova-Koch, T. Muschik, *J. Luminescence* **57**, 271 (1993).
9. T. Maruyama and S. Ohtani, *Appl. Phys. Lett.* **64**, 280 (1994).
10. The system generated 8-ps pulses at 20 Hz, tunable from 0.65 μm (15,400 cm^{-1} /1.9 eV) to 10 μm (1000 cm^{-1} /0.12 eV) with a linewidth of 2 cm^{-1} . The energy per pulse at $\sim 5 \mu\text{m}$ was about 160 μJ [J. Y. Zhang, J. Y. Huang, Y. R. Shen, C. Chen, *J. Opt. Soc. Am. B* **10**, 1758 (1993)].
11. Because the photomultiplier had a cutoff beyond 850 nm, the spectra in Fig. 2, although normalized, may still be somewhat distorted.
12. P. Guyot-Sionnest, *Phys. Rev. Lett.* **67**, 2323 (1991).
13. V.P.K. thanks the Deutsche Forschungsgemeinschaft (DFG) for the Habilitationsspendium. The work of the Berkeley group was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

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Carbon Dioxide Uptake by an Undisturbed Tropical Rain Forest in Southwest Amazonia, 1992 to 1993

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Measurements of carbon dioxide flux over undisturbed tropical rain forest in Brazil for 55 days in the wet and dry seasons of 1992 to 1993 show that this ecosystem is a net absorber of carbon dioxide. Photosynthetic gains of carbon dioxide exceeded respiratory losses irrespective of the season. These gains cannot be attributed to measurement error, nor to loss of carbon dioxide by drainage of cold air at night. A process-based model, fitted to the data, enabled estimation of the carbon absorbed by the ecosystem over the year as 8.5 ± 2.0 moles per square meter per year.

Most of the world's tropical forest is mature and undisturbed, and little is known about its carbon balance. Ecologists consider that in an unvarying environment, undisturbed ecosystems are in a steady state such that photosynthetic gains are balanced

by respiratory losses due to death and decomposition. However, the terrestrial biosphere may be undergoing fertilization as a result of increasing concentrations of CO₂ coupled with higher deposition rates of nitrogen (1, 2). If this is the case, undisturbed tropical forest may be a large sink of CO₂ because of its huge area (3), $10 \times 10^{12} \text{ m}^2$. Now we report direct measurements of CO₂ flux over tropical rain forest in the Brazilian Amazon, to test the hypothesis that virgin forest sequesters carbon from the atmosphere.

We measured fluxes of CO₂, water vapor, and sensible heat over undisturbed forest (4) at Reserva Jaru, Rondonia, Brazil (10°04.84'S, 61°56.60'W), during the dry and wet seasons (September 1992 and April to June 1993, respectively). An eddy co-

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